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Olefins Hydroformylation Reaction Catalyzed by Rhodium Complexes of the Type HRh(P∩P)(CO)$_2$: A DFT and *ab initio* Study

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Abstract: Homogeneous hydroformylation of olefins (convention of alkenes to aldehydes in the presence of CO_2 and H_2) catalyzed by transition metals compounds represents a versatile route for the production of commercially important aldehydes and alcohols, which are difficult to be obtained via conventional synthetic routes. [1] Several organometallic complexes have been used as catalyst for this reaction. Nevertheless, mainly regarding to selectivity of this reaction, catalysts containing phosphines ligands have occupied a central role. [2,3] Studies have showed that coordinating phosphines ligands plays an important role on control of metal´s catalytic activity and selectivity by influencing its electronic and spatial properties. [2,3] Despite the very attractive properties of organometallic compounds with phosphines in the catalysis of the olefins hydroformylation reaction some fundamental questions are not yet fully understood. Specially, concerning to complexes containing phosphines coordinated to metal centers through of bidentate mode, as for instance, the ligands BISBI and DPPE.

In this work, we studied the catalytic cycle of the hydroformylation of propene catalyzed by HRh(BISI)(CO)$_2$ complex. All intermediates and transition states located along the reaction coordinate were obtained at the B3LYP-D2/BS1 of theory. (BS1:Relativistic effective core potential and valence double-ξ basis set of Hay and Wadt was used for Rh atom. The atoms of the ligands were described by using the 6-311G(d) basis set.

Our results show that the propene insertion (first step of catalytic cycle) is the rate-determining step on regioselectivity of the reaction with an activation energy around 22.0 kcal.mol^{-1} for the pathway that leaves to branched product and around 13.0

kcal.mol^{-1} for route that generates the linear aldehyde. Single point energy calculations using several exchange-correlation functional of different approximations (GGA, meta-GGA, Hybrid, double-hybrid and with inclusion of dispersion effects) and the explicitly correlated version of the Möller-Plesset and coupled cluster theories MP2-F12 [4] and CCSD(T)-F12, [5] respectively, were carried out to refine the energetics. The results of this ab initio study as well the details about the DFT calculations will be presented and discussed during the conference.

Key-words: DFT, MP2-F12, CCD(T)-F12, phosphines ligands, hydroformylation

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